

A COMPARATIVE STUDY OF 8 US COALS BY SEVERAL DIFFERENT PYROLYSIS MASS SPECTROMETRY TECHNIQUES

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ABSTRACT

Eight US coals of different rank and/or composition, obtained through the Argonne National Laboratory Premium Coal Sample Program, were analyzed by means of several different pyrolysis-MS (Py-MS) techniques, namely: direct Curie-Point Py-MS, Curie-point Py-GC/MS (including GC/EIMS, GC/CIMS and "short column" GC/CIMS), and vacuum thermogravimetry/MS (TG/MS). The data obtained were compared to Pyrolysis-Field Ionization MS (Py-FIMS) data.

The results show a very good agreement between all techniques used in spite of the marked differences in pyrolysis techniques (Curie-point, furnace, direct probe), "soft" ionization methods (low voltage EI, CI, FI) and mass spectrometer types (quadrupole, ion trap, magnetic sector) used. As might be expected, the most pronounced variations between techniques appear to be due to mass dependent differences in ion transmissivity and detector response, with the type of soft ionization method taking second place and the type of pyrolysis technique showing least effect on the results. Whereas Py-FIMS provides the most complete and detailed overview of the coal pyrolysis tars, Curie-point Py-MS and TG/MS methods provide more reliable information on relatively light gaseous products, and Curie-point Py-GC/MS shows the detail composition of the 2/3 of the total pyrolysis tars.

INTRODUCTION

The extremely complex nature of coal samples necessitates application of a wide range of sophisticated as well as conventional analytical techniques.

Pyrolysis mass spectrometry (Py-MS) is a relatively novel, advanced technique used for studying coals [1-5]. From an instrumental perspective, different Py-MS systems can be distinguished by: (1) pyrolysis technique, such as Curie-point pyrolysis, furnace pyrolysis and direct probe; (2) ionization method, such as electron ionization (EI), low voltage electron ionization (LVEI), Chemical ionization (CI), field ionization (FI), plasma desorption (PD), and fast atom bombardment (FAB); and (3) mass spectrometer type, such as quadrupole, ion trap, electric sector, magnetic sector, time-of-flight, and Fourier transform ion cyclotron resonance.

In this paper, several different Py-MS techniques, namely: direct Curie-point Py-MS, Curie-point Py-GC/MS (including GC/EIMS, GC/CIMS, "short column" GC/CIMS), and vacuum thermogravimetry/MS (TG/MS) were used for studying the 8 US coals from the Argonne National Laboratory Premium Coal Sample Program (ANL-PCSP). The results of a comparison between these methods as well as Py-FIMS will be discussed.

EXPERIMENTAL

Sample Collection and Preparation for Py-MS and Py-GC/MS

All 8 ANL-PSCP coals were obtained as 5 g, -100 mesh aliquots in dark tinted glass ampules closed under argon. The closed ampules were stored at -30 C until used. A 5-10 mg coal sample was suspended in 1-2 ml of Spectrograde methanol (5 mg/ml) and carefully hand-ground to a fine, uniform suspension. Then, a 5 μ l drop of the coal suspension was coated on the pyrolysis wire and air-dried. Next, the coated wire was inserted into a borosilicate glass reaction tube. Details of the sample preparation technique have been described by Meuzelaar et al. [1,6].

Curie-point Py-MS

Curie-point Py-MS was performed with an Extranuclear 5000-1 quadrupole Py-MS system as described previously [3]. The Py-MS conditions are listed in Table 1.

Curie-point Py-GC/MS

The Curie-point pyrolysis reactor [7] was controlled by a Fischer Labortechnik, 1.1 MHz, 1.5 kW high frequency power supply. A HP 5890a gas chromatograph using both regular (15 m) and short (4 m) fused silica capillary GC columns, and coupled directly to a Finnigan MAT 700 ITD mass spectrometer operating in EI or CI (isobutane) mode was used. Experimental conditions are shown in Table 1.

Vacuum Thermogravimetry/MS

Experiments were conducted on a Mettler TA1 thermoanalyzer coupled directly to a Finnigan MAT 3200 quadrupole MS system [5]. Table 1 shows details of the experimental conditions.

Py-FIMS

A Finnigan MAT 731 double-focussing magnetic sector mass spectrometer, a combined EI/FI/FD/FAB ion source and an AMD Intetra direct probe introduction system [8] was used for this experiment. Experimental conditions are given in Table 1.

RESULTS AND DISCUSSION

Figure 1 shows the mass spectra of three coals, Beulah Zap (lignite), Pittsburgh #8 (hvb) and Pocahontas #3 (lvb), obtained by Curie-point Py-MS at ambient inlet temperatures.

The spectra reflect the well-known fact that the pyrolysis products are coal rank dependent. The most prominent products from lignite (Beulah Zap) are oxygen-containing compounds, including (alkyl) phenols, (alkyl) dihydroxybenzenes and (alkyl) methoxyphenols. With increasing rank, the relative abundance of these oxygen-containing compounds decreases. The (alkyl) dihydroxybenzenes and (alkyl) methoxyphenols have nearly disappeared in the Pittsburgh #8 spectrum whereas (alkyl) naphthalene abundances have markedly increased. The most prominent pyrolysis products from Pocahontas #3 coal are aromatic and aliphatic hydrocarbons whereas oxygen-containing compounds are hardly detectable.

All other five Py-MS techniques show a similar rank dependence. With increasing rank aliphatic and aromatic oxygen-containing compounds decrease while aliphatic and aromatic hydrocarbon intensities increase. Rank effects on pyrolysis patterns observed by Curie-point Py-GC/MS, Py-FIMS and TG/MS have been discussed in more detail elsewhere [5,9].

Effect of Pyrolysis Method

Figures 1b, 2 and 3 illustrate the Py-MS patterns of Pittsburgh #8 coal as obtained by Curie-point, furnace and direct probe pyrolysis, respectively. As listed in Table 1, the detailed experimental conditions are quite different from one another, e.g., with regard to sample amount (25 μ g to 5 mg) and heating rate (1,000 C/sec to 25 C/min). However, as seen from Figures 1b, 2 and 3, the three techniques produce rather similar mass spectral patterns in the overlapping mass ranges, viz m/z 50-200. This may imply that the pyrolysis mechanisms are similar under the experimental conditions used.

Effect of Ionization Method

As expected, regular (70 eV) voltage electron ionization methods tend to break molecular ions into smaller fragment ions. Figure 4 shows that the dominant peaks are found at odd mass numbers in the low mass range. The spectra in Figures 1 and 2, however were produced by low voltage EI (12 eV and 14 eV, respectively). Consequently, molecular ions, seen primarily at even mass numbers because of the relatively low fragmentation of compounds as well as a low abundance of nitrogen compounds, dominate. However, as expected the CI spectra in Figures 5 and 6 are dominated by odd mass numbers due to the fact that most molecular ions are protonated $[M+H]^+$ forms. As shown in Figure 3, the FI technique produces largely even numbered molecular ions.

Variations between Methods

Notwithstanding the apparent similarities between the different techniques, as demonstrated in Figures 1-6, there are several other sources of variance that have not yet been discussed.

Except for the differences in pyrolysis techniques and type of quadrupole mass spectrometer used, distances between pyrolysis zone and ion source as well as transfer zone and ion source temperatures are comparable in Curie-point Py-MS and TG/MS techniques. Since, as shown above, differences in pyrolysis techniques appear to have minimal effect on pyrolysis mechanisms, the results from both techniques are quite similar (Figures 1 and 2).

Figure 3 shows the Py-FIMS results. Compared to Curie-point Py-MS and TG/MS, the distance between pyrolysis zone and ionization region is approx. 50% shorter. More importantly, ion source temperatures are higher and we are dealing with a different type of mass spectrometer (magnetic sector vs. quadrupole). Consequently, Py-FIMS detects far more high molecular weight components (Figure 3). Components below m/z 240 constitute only about 10-40% of the total signal intensity, depending on rank. Comparison of Figures 1 and 2, with Figure 3 indicates that Curie-point Py-MS and TG/MS detect only 10-40% of the total pyrolysis products, which agrees with previously published results [1]. The main reasons appear to be: (1) low transmissivity of quadrupole mass spectrometers in the higher mass ranges, and (2) unheated transfer zones and ion sources in the standard Curie-point Py-MS and TG/MS configurations causing condensation losses of large molecules (heating inlet system and ion source markedly increases signal intensities in the higher mass range [10] but also tends to lead to more rapid contamination of the ion source).

Figures 5 and 6 shows the effect of column length on Curie-point Py-GC/MS results. As expected, the use of short capillary GC columns at high linear carrier gas flow velocities enhances the detection of large molecules. The molecular weight averages (Table 2) shift some 15 to 60 mass units towards the high mass range. Compared to Py-FIMS, however, average Py-GC/CIMS molecular weight values are still considerably lower. Currently, efforts are underway to correct the molecular weight profiles obtained by short column Py-GC/CIMS for known differences in ion transmissivity between quadrupole, ion trap and magnetic sector MS systems.

CONCLUSIONS

1. The known rank dependence of coal pyrolysis products is readily detected by all six Py/MS techniques used.
2. Within the range covered by these six techniques, differences in heating rate and sample size do not have a strong effect on the distribution of coal pyrolysis products.
3. All three soft ionization methods used (CI, FI, low voltage EI) appear useful for studying molecular weight distributions.
4. Although the type of pyrolysis method used has little effect on the composition of the pyrolysis products, the choice of the product analytical method has a major influence.
5. Magnetic sector instruments, e.g., as used in FIMS appears to provide the most complete and detailed overview of the coal pyrolysis tars.
6. Py-GC/MS (EI and CI) is capable of providing detailed information on compounds in the molecular weight range up to m/z 400, representing about 2/3 of the total tar.
7. Finally, the information obtained by Curie-point Py-MS and TG/MS methods for high molecular tar products is strongly dependent on inlet and ion source temperatures.

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Table 1. Experimental Conditions

	Py-MS	TG/MS	Py-GC/MS			FIMS
			15m EI	15m CI	4m CI	
Sample Size (g)	2.5×10^{-3}	5.0×10^{-3}	2.5×10^{-5}	2.5×10^{-5}	2.5×10^{-5}	1.0×10^{-4}
Pyrolysis Method	Curie-point	Furnace	Curie-point	Curie-point	Curie-point	direct probe
Final Temp. (C)	610	700	610	610	610	750
Heating Rate (K/sec)	1×10^2	4×10^{-1}	1×10^3	1×10^3	1×10^3	1×10^6
Inlet Temp. (C)	≈ 100	≈ 100	290	290	290	≈ 200
Pressure in Pyrolysis Zone	high vacuum ($<10^{-4}$ torr)	high vacuum ($<10^{-4}$ torr)	30 p.s.i. (abs)	30 p.s.i. (abs)	25 p.s.i. (abs)	high vacuum ($\approx 10^{-5}$ torr)
Distance (from Pyrolysis Zone to Ion Source)	5 cm	5 cm	15 m	15 m	4 m	2 cm
MS Type	quadrupole	quadrupole	Ion Trap	Ion Trap	Ion Trap	magnetic sector
Ionization Method	EI (12 eV)	EI (14 eV)	EI (70 eV)	CI (isobutane)	CI (isobutane)	FI
Ion Source Temp (C)	≈ 100	≈ 100	230	230	230	200
Mass Range Scanned	20-240	33-200	50-450	90-500	100-600	50-900

Table 2. Molecular Weight Averages (\bar{M}_n)
Obtained by Different Techniques

Coal	Curie-point Py-GC/MS		FIMS
	15 m CI	4 m CI	
Beulah Zap	172	185	792
Wyodak-Anderson	184	203	338
Illinois #6	222	270	367
Blind Canyon	226	269	366
Pittsburgh #8	222	264	324
Lewiston-Stockton	218	263	327
Upper Freeport	223	277	386
Pocahontas #3	195	251	359

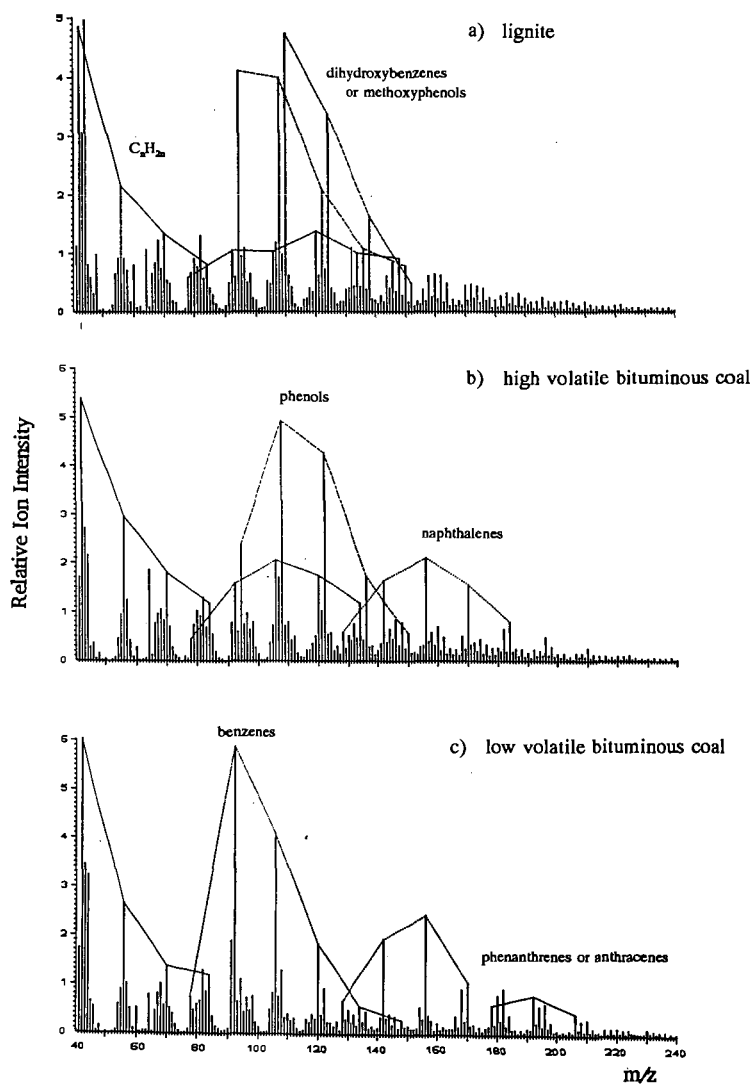


Figure 1. Curie-point pyrolysis low voltage EIMS spectra of a) Beulah Zap lignite, b) Pittsburgh #8, c) Pocahontas #3 coals.

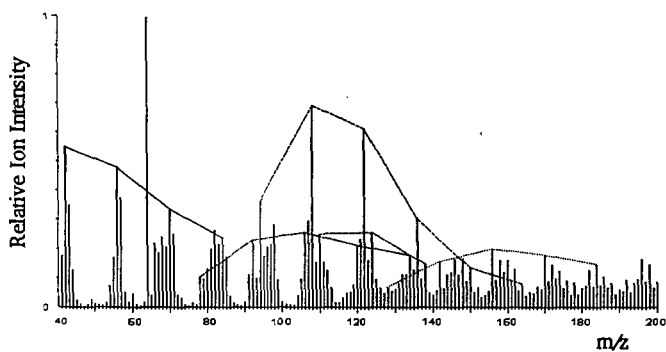


Figure 2. Mass spectrum of Pittsburgh #8 coal by TG/MS.

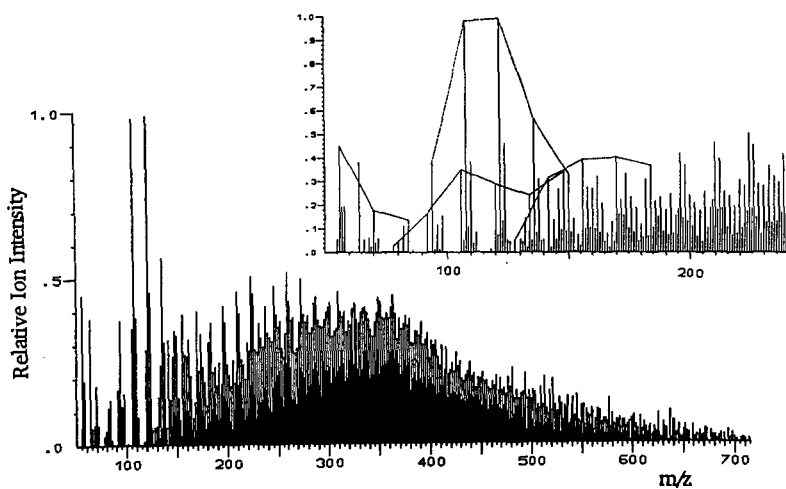


Figure 3. Mass spectrum of Pittsburgh #8 coal by Py-FIMS.

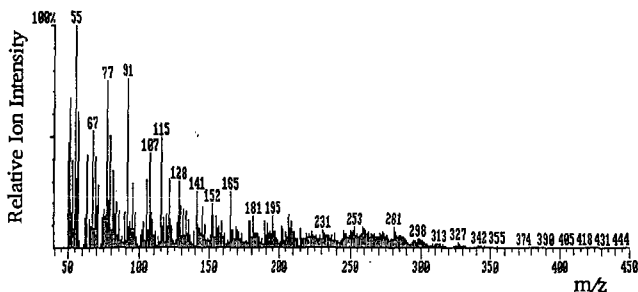


Figure 4. 70 Mass spectrum of Pittsburgh #8 coal obtained by Curie-point Py-GC/EIMS (70 eV).

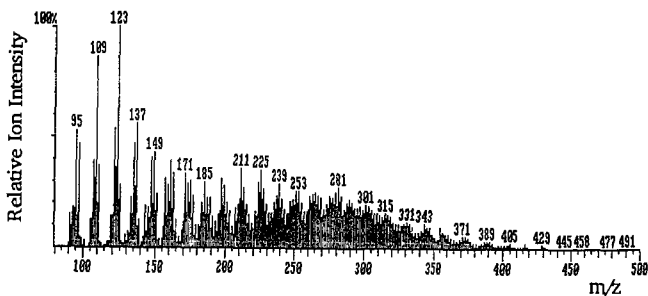


Figure 5. As Figure 4, obtained by Curie-point Py-GC/CIMS.

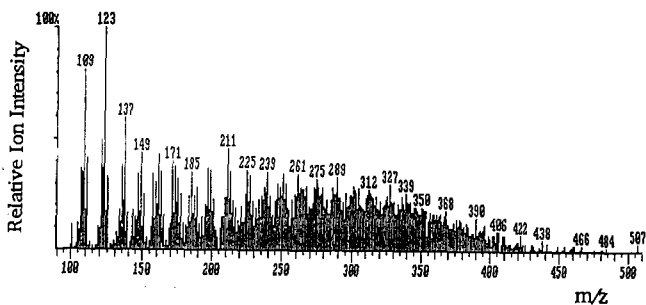


Figure 6. As Figure 4, but obtained by "short column" by Curie-point Py-GC/CIMS.